

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No.: 5253-00001 (FF39046/06)

Applicant(s)	Alexander et al.)	
)	
Serial No:	10/523,164)	Examiner:
)	Robert S Loewe
Confirmation No:	1418)	
)	Art Unit:
Filed:	August 29, 2005)	1796
)	
For:	FIRE RESISTANT SILICONE)	
	POLYMER COMPOSITIONS)	

DECLARATION UNDER 37 CFR § 1.132 OF
PULAHINGE DON DAYANANDA RODRIGO

Commissioner of Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Dear Sir:

I, Pulahinge Don Dayananda Rodrigo; hereby declare:

1. I am the Pulahinge Don Dayananda Rodrigo, named as an inventor in the application.
2. I am qualified as a Materials Scientist having obtained the degree of Doctor of Philosophy (PhD) in Materials Science from the University of Limoges, France, in 1986.
3. My work experience includes over 20 years in the materials industry involved in research and development of ceramic materials. Since 2002 I have been employed as a Senior Research Fellow, at Monash University, Clayton, Victoria, Australia, in which capacity I have conducted research in relation to polymeric compositions filled with inorganic materials, which, in a fire, form a ceramic so as

to provide a barrier to the spread of fire and/or preserve communications cables required for evacuation, or fire fighting in the event of a fire.

A copy of my work listing is enclosed as Exhibit 1 hereto.

4. As a result of my qualifications and work experience, I have attained a high level of knowledge in relation to the chemical and physical properties of ceramics in general and, in particular, filled polymer compositions which form a ceramic residue in a fire.
5. I have read the Examination Report of January 30, 2009, in which the Examiner has rejected the claims.
6. The Examiner has referred to a translation of JP55-078073 (Mizutani et al.) which I have read and understood.
7. Mizutani refers to an option of adding glass frit. The reader of Mizutani is lead by Mizutani to use an amount of glass frit of 15%. In Example 3 on page 14 of the translation (which contains the only teaching regarding the amount of glass frit), Mizutani directs the reader to use 15% of the silicone base composition of phosphate frit having a softening temperature of 650°C. Mizutani also uses a significant amount of devitrified mica glass. Devitrified mica glass prepared by melting a mixture of oxides and a fluoride as described in page 5 (second paragraph) of the translation of JP55-078073 is a synthetic glass ceramic and contains a significant proportion of glass (20% as given in Example 1).
8. It is important to note that the material is prepared as a coating and is therefore diluted with a large volume of solvent. In the examples the composition contains 250 parts 1, 1, 1-trichorethylene as the solvent and 100 parts of other components. In each case, the amount of silicone resin in the coating is 8.6% of the coating composition (30% of composition other than solvent). The phosphate frit is present in an amount of 4.28% of the total coating or 15% of components other than solvent.

9. The Mizutani therefore addresses the approach to fire protection used by Landin et al. in the sense that it uses a system requiring a very large proportion of solvent.
10. The Examiner has considered Mizutani et al. with Takahashi et al. US Patent 5061736 which I have read and understood.
11. Although the two patents (Takahashi et al. and Mizutani et al.) are from the same field of endeavour in the very general sense that they relate to compositions containing silicone rubber for fire protection, they nonetheless disclose very different approaches to the problem of fire protection. Their approaches are so different that their teachings can not sensibly be considered together. They merely provide alternative approaches to fire protection which might be useful in different end uses.
12. As I have discussed above, Mizutani et al. relates to a coating composition containing a large amount (over 70%) of a solvent.
13. Takahashi on the other hand, is concerned with forming a foamed silicone rubber body having a cellular structure. The Takahashi composition therefore needs to form a sufficiently viscous material to trap and support a dispersed gas phase. The presence of large amounts of solvent required by Mizutani et al. are incompatible with forming a foamed composition as solvent in such high proportions will not trap or form a dispersed gas phase with a blowing agent.
14. Takahashi et al. teach a foamed silicone composition which calls for the presence of (b) silica filler, (c) powder of ferrite, (d) flakes of mica or sericite, fibres of ceramics and glass" (e) platinum compound or metal, (f) curing agent for silicone rubber and (g) blowing agent to produce a cellular structure. Although Takahashi component (d) is a material selected from "flakes of mica or sericite, fibres of ceramics and glass" Takahashi et al do not teach the use of mica in combination with glass. Indeed it is clear from the examples that mica and glass are regarded as alternative choices for component (d). The discussion of component (d) in columns 5 and 6 makes it clear that the amount of the

component to be used is different for each of these options. Takahashi et al. at column 6, lines 36 to 41 states that when component (d) is a glass powder the preferred amount is 20 to 200 parts by weight per 100 parts diorgano polysiloxane. Further, the base composition demonstrated by Takahashi (see Example 1 at column 10 lines 5 to 19) does not contain either mica or glass or other option for component (d) and in each of the invention composition of Takahashi one only of the options of component (d) is used and not a combination of glass and mica as required in the present application. Accordingly Takahashi et al have not considered the combination of mica and glass let alone the interaction of glass and mica.

15. The importance of both mica and glass fibre or frit in the present invention and their interaction is discussed in the specification of the present application such as in paragraphs [0025] and [0039].
16. The present application demonstrates in Example 1 that the amount of glass frit and its interaction with mica has a significant effect on the dimensional stability of the silicone compositions in a fire. The following tests were carried out under my supervision in preparation of the present application and in particular Example 1 reported therein:

Specimens of dimensions 38.1 mm x 13.3 mm x 1.7 mm, made from thermally crosslinked (170° C., 30 minutes, 7 MPa) compositions containing the silicone elastomer and peroxide with 20% wt/wt and 30% wt/wt mica and differing levels of a low softening point glass frit, were heated to the temperatures indicated at 10° C. for 30 minutes in air. The percentage changes in volume for the cooled samples are given in Table 1 below. The results show that if the levels of the glass frits are increased to 10%, there is significant shrinkage of the compositions at 1030° C.

TABLE 1

TABLE 1: The effect of mica levels, glass frit levels and firing temperature on percentage volume change.

Composition (% wt/wt)	600° C.	1030° C.
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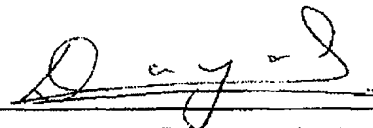
Silicone/mica/peroxide (78:20:2)	+7	+1
Silicone/mica/glass frit A/peroxide (73:20:5:2)	+7	0
Silicone/mica/glass frit A/peroxide (70.5:20:7.5:2)	-1	-7
Silicone/mica/glass frit A/peroxide (68:20:10:2)	+6	-22
Silicone/mica/glass frit A/peroxide (63:30:5:2)	+7	-1
Silicone/mica/glass frit A/peroxide (58:30:10:2)	+2	-45

17. The tests demonstrate that 10% glass frit in the silicone and mica composition produces a significant shrinkage of the material in a fire. The finding of improved dimensional stability for the composition with 0.3 to 8% w/w glass frit or fibre is important finding because dimensional stability is critical for many articles, such as cable, to maintaining effective insulation during a fire. Severe shrinkage, such as 22% or 45% shrinkage in volume exhibited by compositions containing 10% glass frit at 1030°C produces strain in cable insulation layer and other fire barrier articles increasing the incidence of cracking and severely compromising insulation of important communications, power and barrier structures against the fire. In fire situations the effective insulation of communication and power systems against extreme heat and electrical short circuiting is critical to enabling the safe evacuation of people present at the time of the fire and to maintaining the essential systems for fire fighting. The relative dimensional stability of compositions of the invention when compared with corresponding compositions containing more than 8% glass frit or fibre demonstrates a significant improvement in fire protection.

I further declare that all statements made in this declaration of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that wilful false statements may jeopardize the validity of the application or any patent issuing therein.

Date:

20.04.2009



Pulahinge Don Dayananda Rodrigo

⑨ 日本国特許庁 (JP)

⑩ 特許出願公開

⑫ 公開特許公報 (A)

昭55—78073

⑤ Int. Cl.³
C 09 D 5/18
7/12

識別記号

庁内整理番号
7167—4 J
6958—4 J

⑬ 公開 昭和55年(1980)6月12日

発明の数 1
審査請求 有

(全 5 頁)

⑭ 耐熱塗料

大阪市西淀川区千船2丁目14番
16号株式会社ナード研究所内

⑮ 特 願 昭53—152871

⑯ 発 明 者 井沢登一郎

⑰ 出 願 昭53(1978)12月9日

松戸市小金原7丁目25番26号

⑱ 発 明 者 水谷豊信
瀬戸市西松山町221の10

⑲ 出 願 人 大竹碍子株式会社

瀬戸市萩殿町9番地

⑳ 発 明 者 片坂明郷
大阪市西淀川区千船2丁目14番
16号株式会社ナード研究所内

㉑ 出 願 人 株式会社合成化学研究所

東京都千代田区四番町5番地9

㉒ 発 明 者 伊東興一

㉓ 代 理 人 弁理士 鳥居静雄

明 細 書

1. 発明の名称 耐熱塗料

2. 特許請求の範囲

1 少なくとも、シリコーン樹脂とデビトロ化したマイカガラスとを配合して成る耐熱塗料。

2 耐熱塗料はフッ素金雲母を含有して成る特許請求範囲第1項記載の耐熱塗料。

3 耐熱塗料は天然層状構造鉱物を含有して成る特許請求の範囲第1項又は、第2項記載の耐熱塗料。

4 耐熱塗料はガラスフリットを含有して成る特許請求範囲第1項、第2項又は第3項記載の耐熱塗料。

3. 発明の詳細な説明

本発明は、高温領域でデビトロ状セラミック質皮膜を形成することのできる耐熱塗料に関するものである。

従来、300℃以上の高温域において使用ができる耐熱塗料として、ビヒクルにシリコーン系樹脂を用い、これに熱的特性改善のための各種の

無機質粉末を添加した組成物が知られている。無機質粉末の種類としてはアルミニウム、亜鉛のような金属粉末、天然雲母、タルク、モンモリロナイトのような天然層状構造鉱物、その他炭素、炭化物、窒化物、硼化物、けい化物、金属酸化物、ガラス質物のようなセラミック質物がある。

こうした従来のシリコーン樹脂と無機質粉末との組合わせにおいて、耐熱性の向上に一応の効果は認められるが、この場合上記無機質粉末の配合が30%以上になると、被塗装体に形成される塗膜の適性として脆弱化する。とくに塗膜が用途のうえで400℃以上の温度の加熱を受ける場合、ビヒクルであるシリコーン樹脂はその成分中の有機成分が揮散してシロキサン構造(Si-O-Si-O)の無機質物に移行するが、この間シロキサンの結合力は弱く、配合された前記無機質粉末とは何等の結合反応も起きないので、塗膜強度が低下して微細なクラックが発生し、さらに500℃以上になると白炭化や剥離等の劣

化現象があらわれ、耐熱塗膜の性能を失うようになる。

こうした劣化現象の改善法として低融点から高融点にいたるガラスフリットを添加し、シリコーン樹脂のシロキサン化する温度領域(300℃～500℃)でガラスフリットの軟化融解により塗膜の劣化を防ぐ方法が知られている。しかしこの方法による結合の母体はガラス質マトリックスによるものであるため、無機物粉末とのぬれ性、被塗被体との膨張係数差、冷熱の繰返しによるクリープ等が原因となり、ストレスが発生して塗膜は経時的に劣化するようになる。

本発明は上記した従来の耐熱塗料の欠点を改善したもので、少なくとも、シリコーン樹脂とデビトロ化したマイカガラス(以下これをマイカガラスと略称する)とを配合して成る耐熱塗料を特徴とするものである。

本発明はシリコーン樹脂とそれが分解する高温域におけるデビトロ化したマイカガラスとのセラミック化反応により、デビトロセラミック質皮膜

を形成し、長期間にわたる高温域で冷・熱を繰返しても損傷を起こすことがない耐熱塗料を提供しようとするもので、この場合セラミック反応はシロキサンとマイカガラスとの固相体反応であり、従来の天然雲母とシロキサンとガラスフリットとによって形成される単なるガラス融着被膜とは本質的に異なるものである。

デビトロ化したマイカガラスは、 $K_2O-MgO-MgF_2-SiO_2$ 組成による物質で、たとえば $0.5K_2O \cdot 1.5MgO \cdot MgF_2 \cdot 4SiO_2$ のモル比で配合したバッチを少なくとも1300℃以上で溶融し、その溶融体を急冷することによって得られる。たとえば1400℃の溶融体を10～20分で1000℃まで冷却すると、その焼塊の量によっても異なるが、ガラス中に70～80%のカリ四ケイ素雲母($KMg_2Si_4O_{10}(F)_2$)を折出したデビトロセラミックスが得られる。そしてこのデビトロセラミックスは冷却速度が早い程ガラス成分比は多くなる。

マイカガラスはカリ四ケイ素雲母結晶を折出したセラミックスであるので、溶融体は粘度が大き

く、この組成以外のフッ素雲母の成分の溶融体に比べてマイカ結晶の生成がしにくく、過冷却により容易に100%から5%付近までのガラスとなるという特徴をもっている。

本発明において、半融状態で強アルカリ性であるマイカガラスは、シロキサンのような非晶質の SiO_2 分を溶解してガラス化する作用と、600℃付近より揮散する少量のフッ化物、 KF 、 SiF_4 等のガスが SiO_2 の溶融点を低下させる作用とが協同して、900℃付近よりマイカガラスとシロキサンとの焼結が始まる。またマイカガラスは、多くのフッ素雲母や天然雲母等の膨張係数が $10 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ 以上であるのに対して $4 \sim 5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ であるから、マイカガラスの配合された塗膜では急冷に対してストレスが少く損傷を起さない。

本発明においてはシロキサンとマイカガラスとのセラミック化反応を安定に行なわせるとともに、低温域での塗膜の可撓性や高温域での熱的特性を向上させるため、シリコーン樹脂とマイカガラスとの配合物に、フッ素金雲母又は金雲母、白

雲母、パーミキュライトのような天然の層状構造鉱物を添加するのが好ましい。

即ち、上記したシロキサンとの焼結を600℃位から行なわせることができるマイカガラスは、焼結性にすぐれてはいるが、比較的劈開性が小さい。そこでアスペクト比の大きいフレークが塗膜内で被塗被体表面と平行に且つ重なり合って凍結する組織を形成するようにする。

フッ素金雲母はフッ素雲母の代表的な品種であり、結晶性が高く、劈開性が発達しており、粉砕によりアスペクト比50～100程の良好なものが容易に得られる。そしてマイカガラスとは1,100℃付近より固相体間で固溶体を形成しセラミックス化する。これはマイカガラスの半融状態で起きるセラミック化であるので、塗膜は流動せず安定している。また天然雲母等も良好なアスペクト比のフレークが容易に入手でき、塗膜に可撓性を付与するとともに、高温域においてマイカガラスとシロキサンとの間で生成するガラス融液により塗膜組織内で他の成分と融解する。そしてへき開が

良好に行われる天然層状構造鉱物なら、金雲母、白雲母、パーミキュライトをはじめ他の品種のものも使用でき、これらは単独でもフッ素金雲母との併用でも効果上変るところはない。

さらに、本発明においてはシリコン樹脂とマイカガラスとの配合物にガラスフリットを添加することが、好ましい。即ちガラスフリットの添加はセラミック化の過程において、シリコン樹脂のシロキサン化が始まる350℃より、マイカガラスとシロキサンの固着が始まる900℃付近までの焼成のクラックの発生や剝離を防ぐとともに、900℃以上ではフッ素雲母^{字加入}シロキサン系のセラミックス化反応に参加し、デビトロ形式のセラミック皮膜を形成することである。

ガラスフリットの種類としては硫酸塩、硼けい^{字加入}酸塩、^{字加入}硼けい酸塩等が使われる。これらのガラスフリットには軟化点が350℃から900℃位のものがあり、塗膜の使用温度領域や被塗物の材質等により適宜選択する。

マイカガラスは半融状態よりほう酸塩、りん酸

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塩とは相互に融合して界面に新しいガラスを形成する。そしてこの融合ガラスより冷却時カリ四ケイ素雲母の微結晶が析出する。これはいわゆるデビトロセラミックスの形成過程と同様のものである。もちろんフッ素金雲母や天然雲母等とも新しく形成された融合ガラスは密接に融着する。このようにして形成されるセラミック皮膜は、弾性の大きい、アスペクト比の良好なフレークの均質な重なり合いを、デビトロ質のガラスが結合マトリックスとなって緻密でしかも被塗物と強力に結合した組織としたものである。耐熱性であり且つ冷熱サイクルに対してすぐれた耐久力をもつものである。

本発明に用いられるシリコン樹脂の種類はストレートシリコン、変性シリコン或はコールドブレンド型のもののどれが用いられてもよい。しかしその場合、最終的にセラミック^{字加入}反応に参加するシロキサン成分を樹脂以外の無機質物の1/20以上含有することが好ましく、その外の原料等は塗料の使用条件により選択される。すなわち常温

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時は可撓性を保持し、極端な温度変化たとえは火災、落着金属飛沫やアークが融れるような無機繊維布束の塗膜にはシリコンゴム系のものが、また熱硬化処理のできない大きな被塗物たとえは、船舶、内燃機関、炉内構等の不燃化塗料には常成性の他の樹脂とのコールドブレンド型のものが、また使用温度が500℃以上あって始めから本発明のセラミック化反応が行なわれたものを使うような用途ではシロキサン成分の多いシリコン樹脂を使用する。

本発明の配合組成は、シリコン樹脂(固型分換算)5~90%、マイカガラス95~10%の割合を基本とし、これにフッ素金雲母、天然層状構造鉱物、ガラスフリット等を適宜選択して添加するものである。そしてこの組成のほか、着色顔料、體質顔料、金属粉末を~~加えることは塗膜物性を損わない範囲で適宜加えられる。~~^{字加入}

以上説明したように本発明による耐熱塗料は、常温よりシリコン樹脂の分解する温度までの用途にとどまらず、さらに1,000℃までの高温

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領域でも使用できる。この場合組成成分のシロキサンとマイカガラスとの固溶体形成を基本反応とし、これにフッ素金雲母や天然層状構造鉱物、さらにガラスフリットの加ったデビトロ質ガラスを結合マトリックスとしたセラミック皮膜が被塗物に形成されるもので、その皮膜は弾性フレークの重り合った組織であり、可撓性、耐熱衝撃性および長期にわたる冷熱サイクルにすぐれた耐久力をそなえている。

つぎに本発明の耐熱塗料の製造例を示す。

例 1

マイカガラス: 0.5K₂O・1.5MgO・1.1MgF₂・4SiO₂の配合を1,450℃~1,500℃で溶融し、溶融体を空気中で1,000℃までを20分で冷却し、K₂O2.5(Si₄O₁₀)F₂の結晶約80%とガラス質20%の合成塊を得、これを粉砕して原料に供した。

重量比で、シリコン樹脂(信越化学製KR275)を固型分換算で30%、マイカガラス(325メッシュパス)58%、酸化亜鉛6%、顔料セラミックブラック4%、ノニオン系分散剤1.5%及びオク

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チル酸亜鉛 0.5 % の組成物を 100 部とし、炭酸キシレン 300 部の比率による塗料を調製した。

この塗料を $100\text{ mm} \times 100\text{ mm} \times 1.5\text{ mm}$ の鉄板の片面に塗装し、約 60 分間風乾し、ついで温度 180°C で 30 分間加熱して硬化させ、 0.15 mm 厚の塗膜を得た。これを 200°C から 500°C まで 60 分、 500°C から 900°C まで 30 分、 900°C で 30 分の温度条件で加熱した。得られた塗膜は灰黒色の平滑面を持ったセラミック質皮膜であった。これを常温から 400°C の電気炉中に入れて 10 分保持した後、空气中に取り出し、10 分間放冷して 1 サイクルとする冷熱試験を 20 回繰り返したが塗膜には損傷はなかった。

例 2

マイカガラス：例 1 と同じものを使用する。
フッ素金属母：フッ素金属母をボールミルで 48 時間湿式粉砕し、水噴をした後 200 メッシュパスのものを採取した。このものは平均粒径 $58\text{ }\mu\text{m}$ であり、電子顕微鏡写真による観察によればアスペクト比が $50 \sim 100$ の範囲であった。

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度にかり曲げても折目はつかなかった。このテープで耐火電線（架橋ポリエチレン電線 22 mm ）10 本をまとめてテープで 3 重巻きに結束して、ブンゼンバーナーでテープ面が $900 \sim 1000^\circ\text{C}$ 位の温度になるように加熱したが、A、B いずれの塗膜も不燃性で加熱部はセラミックス状の殻皮が形成されていた。

例 3

マイカガラス及びフッ素金属母は例 2 と同一のものを使用した。

(A) 重量比で、シリコン樹脂（信越化学製 KR-275）を固型分換算で 30 %、マイカガラス 325 メッシュパス 25 %、フッ素金属母 200 メッシュパス 25 %、リン酸塩フリット（軟化温度 650°C ）200 メッシュパス 15 %、分散剤 1 % 及び塗装改良剤 1 % の組成物を 100 部とし、これに溶剤として 250 部の 1,1,1-トリクロルエチレンが配合された塗料を調製した。

この塗料を $100\text{ mm} \times 100\text{ mm} \times 1.5\text{ mm}$ の鉄板の片面に塗装し、30 分間風乾した後、 180°C で 30 分

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天然雲母：カナダ、ケベック州産スズオライト（フロゴバイト系）200 メッシュパス、平均粒径 $47\text{ }\mu\text{m}$ であり、電子顕微鏡写真の観察によればアスペクト比は $60 \sim 120$ の範囲であった。

(A) 重量比で、シリコン樹脂（信越化学製 KR-2038）固型分換算で 30 %、マイカガラス 325 メッシュパス 36 %、フッ素金属母 200 メッシュパス 20 %、酸化亜鉛 7 %、顔料フタロシアニンブルー 5 %、分散剤 1 % 及び塗装改良剤 1 % の組成物を 100 部とし、これに溶剤として 250 部の 1,1,1-トリクロルエチレンが配合された塗料を調製した。
(B) 上記 (A) の組成中、フッ素金属母分を天然雲母 200 メッシュパス 20 % で置き換えたもので、その他の組成は (A) と同じものである。

この塗料 A 及び B を電気絶縁用ガラスクロス（JIS R3414）ECG 30A（平織肉厚 0.3 mm ）の片面に 400 g/m^2 の重量でそれぞれ塗布し、30 分風乾した後 180°C で 30 分間加熱して硬化させ、厚さ 0.27 mm の塗膜を形成させて、耐火電線の集束用テープの試料とした。A 及び B の塗装テープは 180°C

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間加熱し硬化させて 0.15 mm の塗膜を得た。この鉄板を電気炉中で 200°C から 500°C まで 60 分、 500°C から 900°C まで 30 分、 900°C で 30 分の温度条件で加熱した。鉄板上の塗膜は乳白色の斑駁状のセラミック皮膜であった。これを 500°C に保持した電気炉中に入れ、10 分間加熱した後、空气中に取り出し 10 分間放冷して 1 サイクルとする冷熱試験を 20 回繰り返したが塗膜に損傷はなかった。
(B) 重量比でエポキシ変性シリコン樹脂（信越化学製 S1001）を固型分換算で 40 %、マイカガラス 325 メッシュパス 20 %、天然雲母 325 メッシュパス 15 %、珪けい酸質（無鉛）フリット（軟化温度 550°C ）15 %、セラミックブラック 325 メッシュパス 8 %、分散剤 1 % 及び塗装改良剤 1 % の組成物を 100 部とし、これにキシレンと MIBK の混合溶剤（7 : 3）250 部が配合された塗料を調製した。この塗料を $200\text{ mm} \times 200\text{ mm} \times 2\text{ mm}$ の銅板の片面に塗装し、2 時間風乾した後、温度 150°C で 30 分間加熱して硬化させた。この塗膜面を $550 \sim 600^\circ\text{C}$ になるようにガスバーナーで

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30 分間加熱して黒色のセラミックス皮膜を形成
させた。これをセラミック皮膜面が常時 300 ～
350 ℃になるようにガス炉で加熱し、それを 300
時間継続したが皮膜にはクラック、剝離等の損傷
は起きなかった。

代理人 島 居 静 雄 島居静雄

DERWENT-ACC-NO: 1980-52610C

DERWENT-WEEK: 198304

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TITLE: Heat-resistant coating compsn.
contg. silicone resin and
dehydrated mica glass

INVENTOR: ITO K; IZAWA T ; KATASAKA M ; MIZUTANI
T

PATENT-ASSIGNEE: GOSEI KAGAKU KENKYUSHO[GOSEN] ,
OTAKE GAISHI KK[OTAKN]

PRIORITY-DATA: 1978JP-152871 (December 9, 1978)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
JP 55078073 A	June 12, 1980	JA
JP 82061296 B	December 23, 1982	JA

APPLICATION-DATA:

PUB-NO	APPL- DESCRIPTOR	APPL-NO	APPL-DATE
JP 55078073A	N/A	1978JP- 152871	December 9, 1978

INT-CL-CURRENT:

TYPE	IPC DATE
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CIPP	C09D5/18 20060101
CIPS	C09D183/04 20060101
CIPS	C09D7/12 20060101

ABSTRACTED-PUB-NO: JP 55078073 A

BASIC-ABSTRACT:

Paint compsn. contains (a) silicone resin, and (b) dehydrated mica glass. Paint can be used at high temp. ?1000 degrees C, and dehydroceramic film is formed by ceramic forming reaction of silicone resin with dehydrated mica glass at a high temp., at which silicone resin is decomposed. Ceramic film formed on a body to be coated has a texture in which elastic flakes stack and has excellent flexibility, thermal impact resistance and durability against cooling-heating cycle.

Specifically dehydrated mica glass has compsn. of $K_2O-MgO-MgF_2-SiO_2$ and is obtd. by melting a batch with molar compsn. of 0.5 K_2 0.1 $MgO.MgF_2.4SiO_2$ at 1300 degrees C and quenching the melt. When the melt at 1400 degrees C is cooled to 1000 degrees C in 10-20 min., dehydroceramic in which 70-80% of potash tetra silicon mica, $KMg_{2.5}(Si_{40}O_{10})F_2$ is deposited in glass can be obtd.

TITLE-TERMS: HEAT RESISTANCE COATING COMPOSITION
CONTAIN SILICONE RESIN DEHYDRATE
MICA GLASS

DERWENT-CLASS: A26 A82 G02 L02

CPI-CODES: A06-A00E1; A08-R06; A12-B01C; G02-A01A; L02-G06;

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:

Key Serials: 0045 0057 0205 0211 0228 0231
1306 2199 2207 2218 2600 2617
2628 2669 2718 2792

Multipunch Codes: 03& 04- 05- 06- 10& 15- 18& 229
250 308 310 331 360 38- 42- 477
504 541 551 556 560 566 656 721
724 03& 04- 05- 06- 10& 15- 18&
229 250 308 310 331 360 38- 42-
477 504 541 551 556 560 566 656
721 724

PTO 09-0355

CC=JP
DATE=19800612
KIND=KOKAI
PN=55078073

HEAT-RESISTANT COATING
[TAINETSU TORYOU]

TOYONOBU MIZUTANI et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. OCTOBER 2008
TRANSLATED BY: SCHREIBER TRANSLATION, INC.

PUBLICATION COUNTRY	(10):	JP
DOCUMENT NUMBER	(11):	55078073
DOCUMENT KIND	(12):	KOKAI
PUBLICATION DATE	(43):	19800612
APPLICATION NUMBER	(21):	53-152871
APPLICATION DATE	(22):	19781209
INTERNATIONAL CLASSIFICATION	(51):	C 09 d 5/18 7/12
PRIORITY COUNTRY	(33):	
PRIORITY NUMBER	(31):	
PRIORITY DATE	(32):	
INVENTOR(S)	(72):	Toyonobu Mizutani Akisato Katasaka Kouichi Itoh Touichiro Izawa
APPLICANT(S)	(71):	Ohtake Glass K.K. Synthetic Chemical Laboratories
DESIGNATED CONTRACTING STATES	(81):	
TITLE	(54):	Heat-Resistant Coating
FOREIGN TITLE	[54A]:	Tainetsu Toryou

Specification

1. Title of Invention

Heat-Resistant Coating

2. Scope of Claims

1. A heat-resistant coating comprised of at least a silicone resin and devitrified mica glass.

2. A heat-resistant coating according to Claim 1, which coating contains fluorine gold mica.

3. A heat-resistant coating according to Claim 1 or 2, which coating contains a mineral with a naturally layered structure.

4. A heat-resistant coating according to Claim 1, 2 or 3, which coating contains glass frits.

3. Detailed Description of the Invention

The present invention pertains to heat-resistant coating capable of forming devitrified ceramic film in a high temperature range.

Compositions employing a silicone resin as a vehicle and various inorganic powders added thereto to improve thermal characteristics have heretofore been known as heat-resistance coatings at higher temperatures of no less than 300°C. The types of inorganic powders used include powders of such metals as aluminum and zinc; such naturally

illegible minerals as natural mica, talc, and montmorillonite; and such other ceramic substances as carbon, carbides, nitrides, borides, silicates, metal oxides, and hyaline substances.

While such heretofore used combinations of silicone resins and inorganic powders are somewhat effective in increasing heat resistance, inorganic powder content of 30% or more causes a decline in the faculty of the coating film formed on the object to be coated. In particular, heating the coating to a temperature of 400°C or higher for application reasons results in the sublimation of the organic components of the silicone resin serving as the vehicle evaporate, and while said components transition into an inorganic substance with a siloxane structure (Si-O-Si-O), the siloxane bonds are weak during this period and no bonding whatsoever occurs with the aforementioned inorganic powders; hence, the coating film strength declines, resulting in the formation of minute cracks. Further, such degradation as chalking and peeling occur at temperatures of 500°C and

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higher, resulting in the loss of performance as a heat-resistant coating film.

A known method for improving on the degradation

phenomenon involves adding glass frits, having melting points ranging from low to high, and preventing the degradation of coating films through the softening and fusing of glass frits in the temperature range wherein silicone resins transition into siloxanes (300°C ~ 500°C). However, because the bonding *illegible* according to this method is dependent on hyaline matrix, such factors as the wettability with inorganic powders, difference in expansion coefficient with the object to be coated, and creeping due to repeated cooling and heating cause stress, resulting in the degradation of the coating film over time.

The present invention improves on the aforementioned problems presented by conventional heat-resistant coating and is characterized by comprising at least a silicone resin and devitrified mica class (hereinafter abbreviated as "mica glass").

The present invention seeks to form a devitrified ceramic coating film by ceramifying a silicone resin with devitrified mica class at a high temperature at which the resin decomposes, thereby providing a heat-resistant coating that is not damaged by repeated heating and cooling over extended period in the *illegible* range, and, the ceramification reaction in this case being a solid phase reaction between siloxane and mica glass, said coating film

is basically different in nature from the simple conventional glass fusion coating film formed from natural mica, siloxane, and glass frits.

Devitrified mica glass is a substance with the composition $K_2O-MgO-MgF_2-SiO_2$ that is obtained by melting a batch with a molar ratio of 0.5 K_2O :1.5 MgO : MgF_2 :4 SiO_2 at a temperature of 1300°C or higher. For example, when a 1400°C melt is cooled to 1000°C in 10 ~ 20 minutes, 70 ~ 80% of devitrified ceramic comprising precipitated potassium tetra silicon mica $[KMg_{2.5}(Si_4)_{10}F_2]$ can be obtained in the glass, though the amount varies depending on the size of the *illegible* cluster. The ratio of said vitrified ceramic to the glass components increases as the cooling rate increases.

Since mica glass is a ceramic formed by the precipitation of potassium tetra silicon mica crystals, the melt thereof is characterized by the fact it is less inclined to generate mica crystals compared to melts comprising fluorine mica of other compositions, and that over-cooling easily results in the formation of 100% to about 5% glass.

In the present invention, the sintering of mica glass and siloxane is caused to start at about 900°C the joint action of the half melted and strongly alkaline mica to

melt and vitrify non-crystalline SiO_2 and of the small amount of gas comprising such substances as evaporated fluorides, KF , and SiF_4 , to lower the melting point of SiO_2 . Further, because the expansion coefficient of mica glass is $4 \sim 5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ as opposed to the $10 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ or higher of numerous other fluorine, natural and other types of mica, coating films containing mica glass are not stressed much by rapid heating and cooling and, therefore, are not damaged.

In the present invention, it is desirable to add a fluorine gold mica or gold mica, white mica, or such naturally layered minerals as vermiculite to the formulation comprising silicone resin and mica glass in order to stably conduct the ceramification reaction of siloxane and mica glass and to improve the flexibility of the coating film in the low temperature range as well as the thermal characteristics thereof in the high temperature range.

This is to say that the aforementioned mica glass, which can be sintered with siloxane from about 600°C , has relatively little cleavability although it excels in sinterability. Hence, the coating film is formed so that the structure thereof is such that the flakes with larger aspect ratios are overlap with each other and are parallel

with the surface of the object to be coated.

Fluorine gold mica being a typical fluorine mica that has high crystallinity and high cleavability, those of a satisfactory aspect ratio of about 50 ~ 100 are easily obtainable by pulverization. Through a solid reaction, mica glass begins to form a solid solution and ceramifies from about 1100°C. Since this ceramification takes place when the mica glass is in a half-melted state, the coating film does not flow and is stable. Flakes with satisfactory aspect ratios are also easily obtainable from natural and other mica, and they impart flexibility to the coating film as well as *illegible* with the other components within the coating film composition due to the glass *illegible* solution produced between mica glass and siloxane at high temperatures. Any naturally layered mineral that can be

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cleaved satisfactorily may be used, examples of which include gold mica, white mica, vermiculite and other types of minerals, and the effect thereof does not change regardless of whether they are used alone or in combination with fluorine fold mica.

In the present invention, it is desirable to add glass frits to the composition comprising silicon and mica glass. This is to say that the addition of glass frits prevents

the peeling of and the occurrence of cracks in the coating film at temperatures from 350°C, when the silicone resin begins to form siloxane, to about 900°C, when siloxane begins to turn into a solid solution, as well as take part in the ceramification reaction of the fluorine mica and the siloxane series at a temperatures of 900°C and higher, thereby forming a devitrified ceramic coating film.

Examples of the types of glass frits used include borates, borosilicates, *illegible*, and sulfosilicates. The softening points of these glass frits range from 350°C to about 900°C and may be selected as necessary, depending on such factors as the temperature range at which the coating film is to be used and the material comprising the object to be coated. Mica glass mutually fuses with borates and phosphates from when it is in a half-melted state. It is from this fused glass that potassium tetra silicon precipitates out during cooling. This is similar to the formation process of the so-called devitrified. Of course, the newly formed fused glass fusion bonds closely also with fluorine gold, natural, and other mica. Because a ceramic coating film thus formed has a composition wherein the homogeneous overlap of flakes with high flexibility and satisfactory aspect ratios are closely and strongly bonded with the object to be coated with the devitrified glass

serving as the bonding matrix, it is heat resistant and has excellent heat-cool cycle endurance.

As regards the type of silicone resin used in the present invention, any of straight silicon, modified silicon, and cold blended types may be used. However, the content of the siloxane that ultimately participates in the ceramification reaction is desirably no less than 1/20 of inorganic substances other than the resin, and other *illegible* are selected depending on the conditions of use for the coating. This is to say that silicon rubbers are used for application on inorganic *illegible* cloth that maintains flexibility at ambient temperatures and is exposed to extreme temperature changes (e.g., coming into contact with sparks of fire, droplets of molten metal, and arc), cold blends with other *illegible* resins are used in fireproofing coating for large objects that cannot be subjected to thermal curing treatment (e.g. ships, internal combustion *illegible*, and *illegible*), and silicone resins with a high siloxane content are used in such applications where the use temperature is 500°C or higher and those that have undergone the ceramification reaction according to the present invention are used from the beginning.

The formulation composition of the present invention is based on combinations of 5 ~ 90% silicon resin (solid base)

and 95 ~ 10% mica glass, to which fluorine gold mica, naturally layered minerals, glass frits, and other substances are added. Color pigments, extender pigments, and metal powders may be added to the composition as needed to the extent they do not undermine the coating film characteristics.

As explained above, the heat resistant coating according to the present invention is not limited to use in temperatures ranging from ambient temperatures to temperatures at which silicone resins decompose, it can also be used in high temperature ranges of up to about 1000°C. In this case, the basic reaction involves the formation of a solid solution of siloxane and mica glass comprising the composition; a ceramic coating film having devitrified glass matrix containing glass frits is formed on the object to be coated; and said coating film has a composition wherein flexible flakes overlap and is equipped with flexibility, heat resistance, shock resistance, and endurance against heating-cooling cycles repeated over prolonged period.

Working examples of heat-resistant coating according to the present invention are shown hereinbelow.

Example 1

Mica Glass: A 0.5 K₂O:1.5 MgO:L1MgF₂:4 SiO₂ formulation was

melted at 1,450°C ~ 1,500°C, the melt was cooled in air to 1,000°C in 20 minutes, a synthetic clump containing approximately 80% of $\text{KMg}_{2.5}(\text{Si}_4)_{10}\text{F}_2$ crystals and 20% of glass was obtained, and said clump was pulverized for use as raw material.

A coating was prepared with, on the basis of weight, 300 parts of xylene as the solvent and 100 parts of a composition comprising 30% silicone resin (solid basis; KR275 of Shin Etsu Chemical Co., Ltd.), 58% mica glass that passed through a 325 mesh, 6% zinc oxide, 4% black pigment ceramic, 1.5% non-ion dispersing agent, and 0.5% zinc octylate.

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Said coating was applied on one surface of an iron sheet 100 mm x 100 mm x 1.5 mm in size, blow dried for approximately 60 minutes, and subsequently cured by heating at 180°C for 30 minutes to obtain a coating film 0.15 mm in thickness. It was heated from 200°C to 500°C in 60 minutes, from 500°C to 900°C in 30 minutes, and at 900°C for 30 minutes. The coating film obtained was a ceramic film having a smooth surface and grayish black in color. A heating-cooling test was performed, wherein placement in a 400°C electric furnace for 10 minutes, removal therefrom into air, and cooling as is for 10 minutes constituted one

cycle. Although the test was repeated for 20 cycles, no damage was observed on the coating film.

Example 2

Mica Glass: The same one as in Example was used.

Fluorine Gold Mica: Fluorine gold mica was wet milled in a ball mill for 48 hours, water *illegible*, and said mica that passed through a 200 mesh was collected. The average particle diameter of the mica was 58 μ , and the aspect ratio in the 50 ~ 100 range according to the observation of an electron micrograph.

Natural Mica: Tinolite (a phlogopite) from Quebec, Canada that passed through a 200 mesh. The average particle diameter was 47 μ , and the aspect ratio in the 60 ~ 120 range according to the observation of an electron micrograph.

(A) A coating was prepared with, on the basis of weight, 250 parts of 1,1,1-trichlorethylene as the solvent and 100 parts of a composition comprising 30% silicone resin (solid basis; KR-2038 of Shin Etsu Chemical Co., Ltd.), 36% mica glass that passed through a 325 mesh, 20% fluorine gold mica that passed through a 200 mesh, 7% zinc oxide, 5% phthalocyanine blue pigment, 1% dispersing agent, and 1% coating film modifier.

(B) Of the composition in (A) above, the fluorine gold mica

was replaced with 20% natural mica that passed through a 200 mesh. The rest of the composition is the same as in (A).

Coating A and B were each applied on one surface of an electrical insulating glass cloth (JIS R3414) ECG 30 A (plain woven, 0.3 mm in thickness) in an amount of 400 g/m², blow dried for 30 minutes, subsequently cured by heating at 180°C for 30 minutes to form a coating film 0.27 mm in thickness, and the film was used as a sample bundling tape for fire-resistant electrical wires. Coated tapes A and B did not develop a fold, even when bent at a 180° angle. 10 heat-resistant electrical wires (22 ml of cross-linked polyethylene electrical wires) were bundled together and wrapped three times with the tape and heated with a Bunsen burner so that the surface temperature of the tape reached about 900 ~ 1,000°C. Coating films A and B were both nonflammable, a ceramic film had developed on the heated area.

Example 3

The same mica glass and fluorine gold mica as in Example 2 were used.

(A) A coating was prepared with, on the basis of weight, 250 parts of 1,1,1-trichlorethylene as the solvent and 100 parts of a composition comprising 30% silicone resin (solid

basis; KR-275 of Shin Etsu Chemical Co., Ltd.), 25% mica glass that passed through a 325 mesh, 25% fluorine gold mica that passed through a 200 mesh, 15% phosphate frit (softening temperature of 650°C) that passed through a 200 mesh, 1% dispersing agent, and 1% coating film modifier.

Said coating was applied on one surface of an iron sheet 100 mm x 100 mm x 1.5 mm in size, blow dried for approximately 30 minutes, and subsequently cured by heating at 180°C for 30 minutes to form a coating film 0.15 mm in thickness. The iron sheet was heated in an electrical furnace from 200°C to 500°C in 60 minutes, from 500°C to 900°C in 30 minutes, and at 900°C for 30 minutes. The coating film on the iron sheet was an enamel-like ceramic film that was milky white in color. A heating-cooling test was performed, wherein placement in a 500°C electric furnace for 10 minutes, removal therefrom into air, and cooling as is for 10 minutes constituted one cycle. Although the test was repeated for 20 cycles, no damage was observed on the coating film.

(b) A coating was prepared with, on the basis of weight, 250 parts of combined xylene-MIBK solvent (7:3) as the solvent and 100 parts of a composition comprising 40% epoxy-altered silicone resin (solid basis; 81001 of Shin Etsu Chemical Co., Ltd.), 20% mica glass that passed

through a 325 mesh, 15% natural mica that passed through a 200 mesh, 8 % ceramic black that passed through a 325 mesh, 1% dispersing agent, and 1% coating film modifier. Said coating was applied on one surface of a copper sheet 200 mm x 200 mm x 2 mm in size, blow dried for approximately 2 hours, and subsequently cured by heating at 150°C for 30 minutes. The coated surface was heated with a gas burner for 30 minutes so that the surface temperature will reach from 550°C ~ 600°C, and thereby formed a black ceramic coating film. Although it was heated in a gas furnace so

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that the surface of the ceramic coating film will be 300°C ~ 350°C at all times for 300 hours, the coating film did not show any signs of damage, such as cracks and peeling.



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PVB film for laminated safety glass

Glass

Borosilicate glass

Borosilicate glass is a high silicate glass with at least 5% boron oxide bow handle threaded rod with a triangular shaped handle.



Borosilicate glass is a particular type of glass, better known under the brand names Pyrex and Kimax. It was first developed by German glassmaker Otto Schott in the late 19th century and sold under the brand name "Duran" in 1893. After Corning Glass Works developed Pyrex in 1924, it became a synonym for borosilicate glass in the

English-speaking world.

Borosilicate glass is the oldest type of glass to have appreciable resistance to thermal impact and higher temperatures, also has excellent resistance to chemical attack. In this glass structure, the first to carry the Pyrex trademark, some of the SiO_2 is replaced by boric oxide.

Borosilicate glass has a low coefficient of thermal expansion and is, thus, suited for telescope mirrors and other precision parts. Also, because this glass can withstand thermal shock, it is used for oven and laboratory ware, headlamp lenses, and boiler gage glasses. Most borosilicate glasses have better resistance to acids than do soda-lime glasses, but poor resistance to alkalis. Glass fibers used in reinforcing plastic compounds are a modified borosilicate glass.

Chemical Composition

SiO_2 = 80.6%

B_2O_3 = 13.0%

Article

Other Net Sources

Description of Glasses Used in Corning Labware
Technical information

Our publications

Borosilicate Glass Manufacturers
Take a look into the GOW's Suppliers Directory

Explore glass chemical composition
Chemical composition.

Na₂O = 4.0%

Al₂O₃ = 2.3%

Physical Properties

Coefficient of expansion (20°C–300°C) $3.3 \times 10^{-6} \text{ K}^{-1}$

Density 2.23g/cm³

Refractive index (Sodium D line) 1.474

Dielectric constant (1MHz, 20°C) 4.6

Specific heat (20°C) 750J/kg°C

Thermal conductivity (20°C) 1.14W/m°C

Poisson's Ratio (25°C – 400°C) 0.2

Young's Modulus (25°C) 6400 kg/mm²

Optical Information

Refractive index (Sodium D line) = 1.474

Visible light transmission, 2mm thick glass = 92%

Visible light transmission, 5mm thick glass = 91%

Critical Temperatures

150°C - When working above this temperature care should be taken to heat and cool Borosilicate glass in a slow and uniform manner.

500°C - The maximum temperature that Borosilicate glass should be subjected to and then only for short period of no longer than a few minutes.

510°C - Temperature at which thermal stress can be introduced to Borosilicate glassware.

565°C - Annealing temperature. When uniformly heated in controlled conditions, such as a kiln or oven thermal stress's can be removed.

820°C - Softening point at which Borosilicate may deform.

1252°C - Working point, the temperature that glassblowers need to attain in order to work Borosilicate glass.

Working Temperatures

Borosilicate glass retains its mechanical strength and will deform only at temperatures which approach its strain point. The practical upper limit for operating temperatures is much

lower and is controlled by the temperature differentials in the glass, which depend on the relative temperatures of the contents of the equipment and the external surroundings.


Provided borosilicate glass is not subjected to rapid change in temperature, creating undue thermal shock, it can be operated safely at temperatures up to 450°F (232°C). The normal limiting factor is actually the gasket material. The degree of thermal shock (usually defined as sudden chilling) which it can withstand depends on many factors, for example: stresses due to operating conditions; stresses imposed in supporting the equipment; the wall thickness of the glass, etc. It is therefore undesirable to give an overall figure but, as a general guide, sudden temperature changes of up to about 216°F (120°C) can be accommodated.

At sub-zero temperatures, the tensile strength of borosilicate glass tends to increase and equipment can be used with safety at cryogenic temperatures.

Further development in glassmaking continues to create new glass-ceramics that outperform borosilicate glass in various ways.

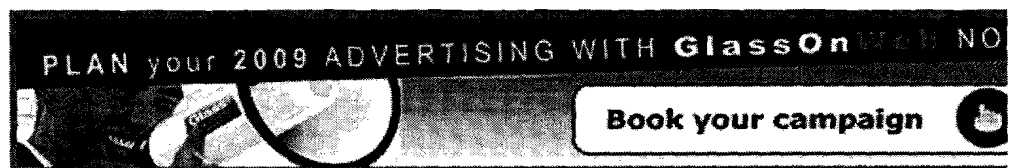
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